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Mechanism and energetics for step merging on a metallic surface captured with scanning tunneling microscopy

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Abstract

Scanning tunneling microscopy has been used to observe oxygen induced microfaceting of Ni(977) in the temperature range of 390–565 K. Step doubling occurs on this surface provided the step-edges are locally decorated with oxygen. In this letter, time-lapse images of this process have been used to resolve two key steps of the coalescence mechanism. Merging of steps is initiated by the bulging of one step in the downstairs direction towards its neighbor. This rate limiting step is followed by the second mechanistic process, namely zippering of adjacent steps. Merging step contact angles have been analyzed to extract information on the energetics of step–step interactions. These results give a real-space view of the atomic-level surface structural changes which accompany the initial stages of metallic oxidation of interfaces containing extended surface defects. © 2001 Published by Elsevier Science B.V.

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Monitoring of surface structural phase transitions with local probes has illuminated many of the issues that influence the delicate balance of surface free energy and orientational instability [1]. Only recently have the factors that govern equilibrium crystal shape [2] and the mechanistic details for surface mass transport been studied using scanning probe instruments [3]. Vicinal (stepped) surfaces have been observed to undergo a wide variety of surface reconstructions and structural

phase transitions [4]. Changes range from irreversible faceting of the surface, i.e. alteration of crystallographic geometry, to more subtle modifications of step–step interaction energetics. While kinetics measurements for dynamical processes such as faceting, step bunching, and other coalescence events have been realized [5] and a great deal of effort has been directed toward understanding the energetics involved in stepped surface structure [6,7], little has been uncovered experimentally regarding the mechanistic details for how two steps merge. In this letter we report real-time, elevated temperature scanning tunneling microscopy (STM) data that furthers our understanding of surface morphological evolution. By monitoring step merging events for this adsorbate driven surface reconstruction on Ni(977) in real-time, we

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demonstrate that the coalescence mechanism consists of two clearly resolved processes, step bulging leading to adjacent step contact followed by zippering. This experiment is part of a larger study in our group and elsewhere, including experiments involving both real and reciprocal space techniques, and theory directed at comprehending the role of defects in metallic oxidation as well as other surface reaction processes [3,8–12].

Experiments were performed in an ultrahigh vacuum chamber with a base pressure of 5.5×10^{-11} Torr equipped with an STM capable of elevated temperature imaging (RT to 650 K) [13] and standard sample cleaning and characterization tools. The Ni(977) surface is a 7.01° miscut of a Ni(111) crystal in the $[2\bar{1}\bar{1}]$ direction. In its unreconstructed step arrangement, this kinkless vicinal is comprised of eight atomic row wide terraces of (111) symmetry separated by monatomic (100) step risers. Sample preparation involved cycles of 1 keV Ar⁺ sputtering between 300 and 1100 K and annealing by electron bombardment at 1100 K. Surface cleanliness was checked by Auger electron spectroscopy, and crystallinity verified using low energy electron diffraction (sharp splitting of the (111) spots) and STM. Elevated temperature dynamics measurements of the surface reconstruction using STM were made between 390 and 470 K. This was achieved by irradiating the rear of the sample; details regarding the experimental setup and imaging techniques at elevated temperature are found elsewhere [13].

Once a well ordered region of single steps exhibiting a narrow terrace width distribution (~ 16.5 Å) was found, imaging would be paused, oxygen dosed by chamber backfilling, and imaging resumed when the exposure was complete. A 1000×1000 Å² region would be imaged for approximately 1 h at elevated temperature immediately after dosing oxygen, where images were recorded every 20–40 s. Image sequences were then compiled into movies, with minor drift corrections, and played at faster frame speeds than the real-time acquisition rates in order to facilitate visual inspection of step coalescence behavior. A number of different observations regarding doubling could be made simply from viewing the steps in fluid motion as opposed to studying consecutive images

statically. For ideal temperature and oxygen conditions, pairs of steps would begin merging regardless of what might be happening to other regions of the step array. Complete titration of the single step density with oxygen, corresponding to every other step-edge site occupied, was found to enable step coalescence to happen most rapidly. Further details regarding the influence of step-edge oxygen concentration on the rate of step merging have been published elsewhere [14,15]. Merging of a pair of steps that started in the imaging area, or that traveled into the STM field-of-view after starting elsewhere, were observed to proceed at a relatively constant areal sweep rate of ~ 60 Å² s⁻¹ [15]. Coalescence advanced in both directions orthogonal to the step-edge normal. A given pair of steps would only stop merging if it encountered a merging mismatch where one step started merging with both of its neighbors at two well separated points along its world line.

Joining of steps proceeds without any long-range correlation between nearby steps. The lack of communication or correlation between different regions might be due to the relatively large size of the terraces involved in our system. A vicinal system composed of fewer atomic rows on its terraces and more step-edges per unit area may exhibit more long-range influences on how the surface free energy is minimized and mechanical stress is relieved. Selected frames from one of the movies are shown in Fig. 1 where a height profile illustrates the ability to distinguish between single and double steps. Arrows in Fig. 1 illustrate the direction of coalescence for individual events showing zippering in both step-edge directions.

By zooming in on an individual pair of merging steps the details of how the doubling process begins have been obtained. Fig. 2 shows three panels that illustrate the need for point contact and subsequent zippering of the steps once contact is made. Initial contact between one step and its neighbor is always made in the downstairs direction of the step train. Connections between steps are not established by negative kinks in the upstairs direction but rather they always occur as positive expansions of the step-edge traversing the terrace and making contact with its neighbor. Calculations by Liu et al. for diffusion mechanisms

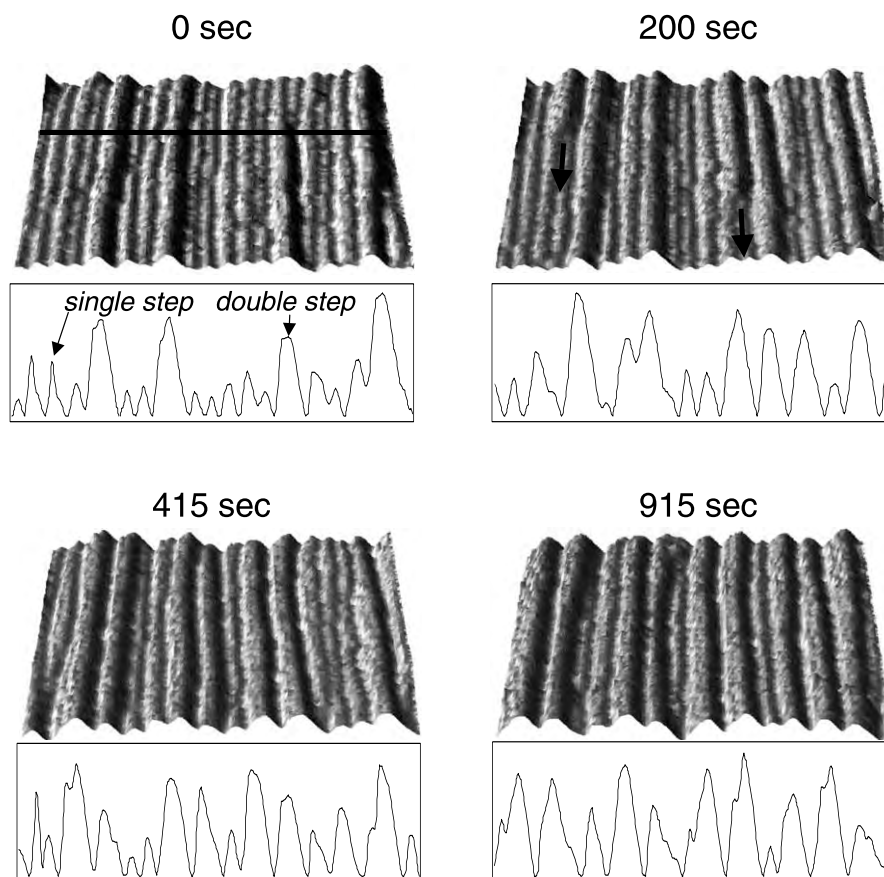


Fig. 1. Time lapsed tracking of step doubling at 440 K and 0.15 L O₂ exposure for a $400 \times 400 \text{ \AA}^2$ area. The four panels and their accompanying height profiles (for the representative line drawn in the first panel) illustrate the structural evolution as well as the ability of the STM to distinguish between single and double height structures at elevated temperature. Two illustrative coalescence events are highlighted in the second panel with arrows that indicate the direction of zippering for those particular examples. The exposure chosen is not random, but corresponds roughly with the density of step-edge sites available (15% of the surface for Ni(9 7 7)); this exposure facilitates the most rapid step coalescence.

on stepped Ni surfaces by embedded atom method show that migration of an adatom away from a kink site, either along the step-edge or out onto the terrace, occurs with a significant energy cost, 0.72–0.79 eV/atom [16]. Mass exchange processes for a fluctuating step-edge have been well characterized and reviewed [3,17]: (1) periphery diffusion where atoms flow along the step-edge only; (2) terrace diffusion in which an atom separates from the step-edge to the terrace, diffuses, then re-attaches at a different position on the step-edge; (3) attachment–detachment mechanism where atoms exchange between the step-edge and the terrace with no

correlation between motion at different sites. Time correlation functions, $G(y, t)$, for fluctuations of individual step-edges as a function of temperature would need to be calculated in order to determine precisely which transport mechanisms are dominating the process. The activation energy extracted from the kinetics measured on this system with STM (0.88 eV) [14] suggests that step-edge mobility leading to bulging is rate limiting in the doubling process. Once a point contact is made then relatively quick zippering of the steps ensues where the new step-edge for the merged pair is at roughly the position of the downstairs step-edge.

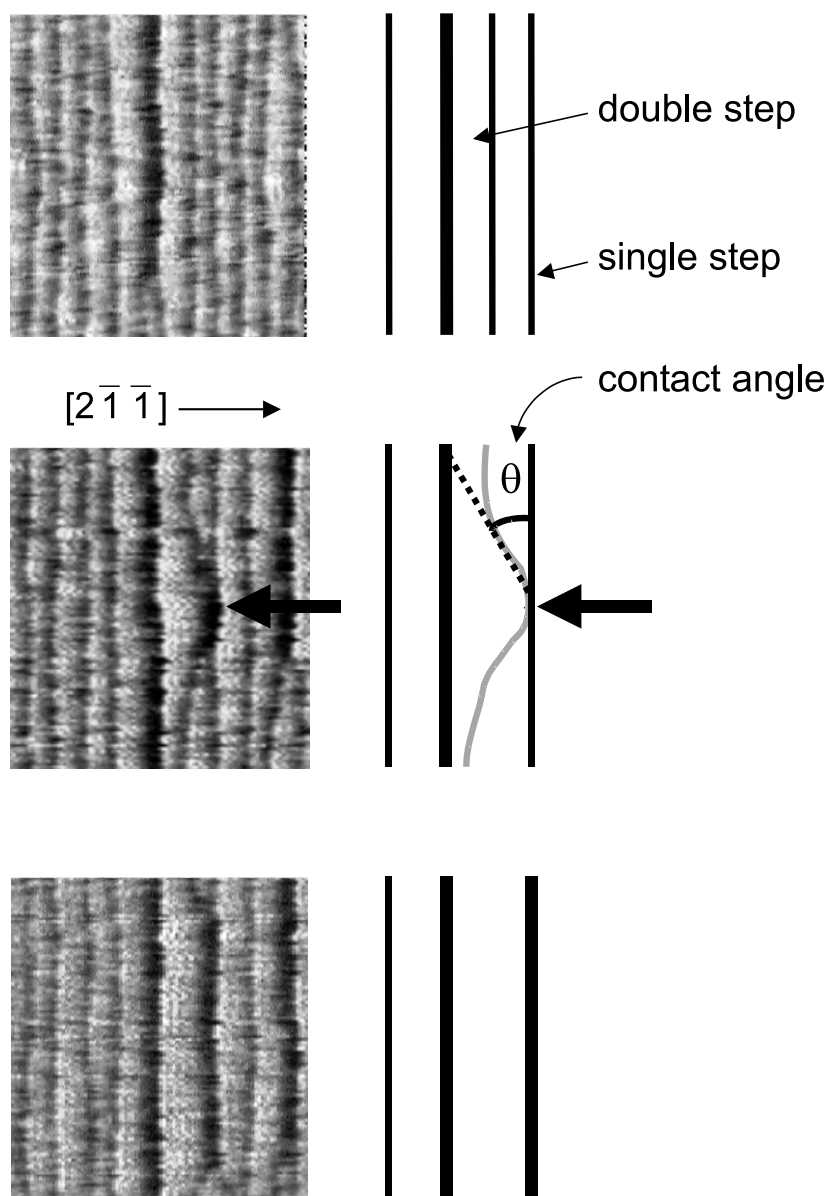


Fig. 2. An individual step merging event resolved in time where the three-frame sequence illustrates mechanistic steps of point contact to zippering in both directions along the step-edge. $350 \times 350 \text{ \AA}^2$ image area shown with approximately 180 seconds between frames with $T_{\text{xtal}} = 470 \text{ K}$ and 0.75 L O_2 exposure. The contact angle between joining steps used for extracting step attraction energetics is also illustrated. Black arrows highlight the step bulge leading to contact made in the downstairs direction. Lines drawn to the side of each image highlight the single (thin) and double (thick) steps along with the initiation of a step merge leading to zippering.

The third panel in Fig. 2 illustrates where the position of the new double step is with respect to the previous single steps. It is not surprising that all of the step merges occur in the same direction and

that they proceed downstairs. If an array of steps were to double perfectly, then the steps would need to perform their merges in the same fashion so as to conserve crystallography. For step joining to be

initiated in the upstairs direction, adatoms would need to overcome the Ehrlich–Schwoebel barrier [18,19] at the top of the step-edges to diffuse across the upper terrace. This zippering of steps is different from step-edge atoms gradually diffusing or percolating across the terrace, and agrees with step doubling modeling performed by Khare et al. [10]. Fig. 3 illustrates the two steps in the coalescence progression.

STM images of the step merging inception enable us to assess relevant energetic parameters since the contact angle, θ , made between two merging steps corresponds to an energetic minimum [20]. When a step-edge makes contact with a (100) step face, the local surface free energy will be determined by the competition between energy gained from the attractive interaction in forming the (100) microfacet, and the energy lost from increasing the step-edge length. The attractive energy associated with the merging of the steps, E_a , can be expressed in terms of the step formation energies for single and double steps, β_1 and β_2 , at a contact angle of θ :

$$E_a = 2\beta_1(0) - \beta_2(0) \quad (1)$$

In order for a double step to be stable, the step formation energy for a double step must be less than twice the energy cost for a single step. In the case where two steps are merging at a contact angle of θ , the step formation energy for the double step corresponds to

$$\beta_2(0) = \beta_1(0) + \beta_1(\theta) \cos \theta \quad (2)$$

and in the limit of small contact angles, $\beta_1(\theta) \approx \beta_1(0)$. This results in an equation for attractive energy of

$$E_a = \beta_1(0)(1 - \cos \theta) \quad (3)$$

The contact angle for both the initial contact of two steps and the geometry of the leading edge of a step zippering event were found to be the same: an angle of 8–15° was typical for merging events. Recent calculations by Vitos et al. on surface free energies for clean flat and vicinal metallic systems yield a step formation energy for a monatomic step, $\beta_1(0)$, on a Ni(111) \times (100) vicinal as 165 meV Å⁻¹ [21]. Using this value as an approximation for the step formation energy of an oxygen

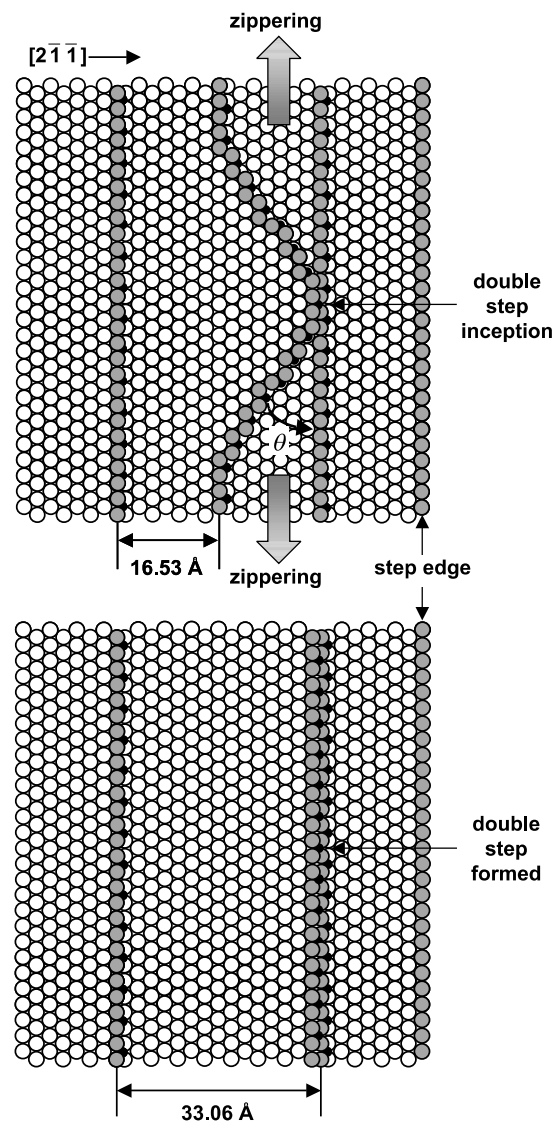


Fig. 3. Top view schematic drawing of the step merging process. Filled black circles correspond to the oxygen atoms that preferentially bind in the fourfold hollow sites available in the (100) microfacets. Coalescence begins with a localized bulge in the downstairs direction ($[2\bar{1}\bar{1}]$) and then proceeds via zippering in both step-edge directions. The contact angle drawn in the figure has been exaggerated for clarity. The local oxygen decorated step-edge structure impacts the likelihood of a step merge as well as the subsequent rate of coalescence.

covered single step and an average contact angle of 10° in the formation of a double step, Eq. (3) yields an attractive energy of 2.5 meV Å⁻¹. This relatively

low attractive energy due to the shallow contact angle indicates that the creation of a double step is primarily driven by the thermodynamically favorable formation of oxygen covered (100) step faces [22]. Step quadrupling has not been observed in our data sets. We attribute this to the thermodynamic stability of the oxygen covered double steps, as well as and perhaps more importantly, the very slow kinetics such doubled structures bulge and migrate across terraces at the temperatures used. At higher temperatures we have previously noted that the oxygen dissolves into the bulk and the driving force for coalescence goes away [9,23]. Finally, the stabilization effect of the oxygen is different from the entropic doubling observed on W(430) [24] and the faceting on vicinal Si(113) [5] induced by short range repulsions at high temperatures.

We have been able to directly observe the oxygen induced merging of steps at elevated temperature using STM. Step coalescence starts by one step making contact with its downstairs neighbor in a spatially localized bulge. Rapid zippering of two steps proceeds after the initial contact is made and continues provided local oxygen concentration conditions at the step-edge are sufficient to drive the transition and no step merge mismatches are encountered. By using contact angle measurements for step merges, we have been able to extract information regarding the impact that the oxygen is making on enabling coalescence to proceed. This mechanism is thought to be universal with respect to faceting and other step joining transitions observed on many vicinal systems. This long-standing issue has been unambiguously resolved with the use of real-space and real-time imaging of a prototypical surface reconstruction. Both reciprocal space helium diffraction [9] and related modeling [10] have suggested this zippering mechanism; these local probe observations confirm this conclusion. These results directly apply to our understanding of adsorbate and substrate interactions with respect to equilibrium morphology, giving insights into the early stages of metallic oxidation. Moreover, these studies illustrate that substrates, and steps in particular, are dynamic during reaction conditions and cannot be treated

statically especially with regard to surface catalytic processes.

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